

# METHOD FOR MEASURING THICKNESS OF OXIDE FILM

## CROSS REFERENCE TO RELATED APPLICATION

This application is based upon and claims the benefit of  
5 Japanese Patent Application No. 11-203562 filed on July 16, 1999,  
the contents of which are incorporated herein by reference.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

10 This invention relates to a method for measuring a thickness  
of an oxide film formed on a substrate, which is suitably applied  
for evaluating a thickness of a transistor gate oxide film.

### 2. Description of the Related Art

Recently, a thickness of a MOS transistor gate oxide film  
15 in an LSI has been thinned to be less than 100Å to comply with  
requirements for an improved integration density and an increased  
speed. Therefore, it has been required and examined to measure  
the thinned gate oxide film accurately in view of reducing a  
measurement error. Widely known methods for measuring a thickness  
20 of a gate oxide film are an ellipsometry utilizing a polarization  
analysis, a nano-spectroscopy utilizing an optical interference  
method, and the like ("University Course of Electricity Institute,  
Electronic Material Engineering", P. 228-231, written by Institute  
of Electricity Communicational Education, and "Applied Physics  
25 Selection, 3. Thin Film", P. 200 to 203, written by S. Kanbara  
and H. Fujiwara). In the ellipsometry, light is irradiated on  
the gate oxide film by an optical instrument to detect a refractive

index and an absorption coefficient, and the thickness of the gate oxide film is measured based on the refractive index and the absorption coefficient.

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#### SUMMARY OF THE INVENTION

However, when the thickness of the gate oxide film was measured by the conventional optical instrument, large variations beyond measurement errors of the optical instrument occurred. The large variations make measurement and control of the gate oxide film thickness inaccurate and difficult.

The present invention has been made in view of the above problem. An object of the present invention is to provide a method for measuring a thickness of an insulating film. Another object of the present invention is to control and evaluate an insulating film easily.

According to a first aspect of the present invention, a thickness of an oxide film is measured by controlling a left period of time for leaving the oxide film from the formation of the oxide film to the measurement of the thickness. As a result, the thickness can be measured accurately. The measured thickness may be corrected in accordance with the left period of time.

According to a second aspect of the present invention, a thickness of an oxide film is measured after washing a surface of the oxide film. The washing of the oxide film removes deposits from the surface of the oxide film, resulting in accurate measurement of the thickness of the oxide film. The left period of time for leaving the oxide film from the washing to the

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4.2  
cont  
measurement of the thickness can be controlled to more precisely  
measure the thickness.

When the method for measuring the thickness of the oxide film according to the present invention is performed on the way of manufacturing a semiconductor device, a defective can be found out on the way of manufacture by determining whether the thickness of the oxide film falls in a desirable range or not. A succeeding step is performed when the thickness falls in the desirable range.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and features of the present invention will become more readily apparent from a better understanding of the preferred embodiments described below with reference to the following drawings, in which;

FIGS. 1A to 1C are cross-sectional views showing manufacturing steps for a MOS transistor to which a method for measuring a thickness of a gate oxide film is applied in a first preferred embodiment;

FIGS. 2A to 2C are cross-sectional views showing manufacturing steps for the MOS transistor, following the step shown in FIG. 1C;

FIG. 3 is a graph showing a relation between an apparent thickness of the gate oxide film and a left period of time elapsed from the formation of the gate oxide film;

FIG. 4 is a graph showing thicknesses of the gate oxide film, corrected by an approximate formula, in a second preferred embodiment;

FIG. 5 is a graph showing a relation between a thickness of the gate oxide film determined by the approximated formula, and a thickness of the gate oxide film calculated based on a capacitance;

5        FIG. 6A is a graph showing a change in thickness of the gate oxide film before and after washing is performed using a mixed solution of sulfuric acid ( $H_2SO_4$ ) and hydrogen peroxide ( $H_2O_2$ ) in a third preferred embodiment; and

10        FIG. 6B is a graph showing a change in thickness of the gate oxide film before and after washing is performed using a mixed solution of hydrochloric acid (HCl) and hydrogen peroxide ( $H_2O_2$ ) in the third embodiment.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

15        (First Embodiment)

In a first preferred embodiment, a method for measuring an oxide film thickness according to the present invention is applied to a manufacturing process for a MOS transistor. Specifically, in a manufacture line for a product including a MOS transistor, a thickness of an oxide film formed therein is measured. If the thickness falls in a desirable range, the next step is performed. If the thickness is out of the range, the produce is removed as a defective.

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The method for measuring the thickness of the oxide film is specifically explained referring to FIGS. 1A-1C and 2A-2C below. First, as shown in FIG. 1A, a thermal oxide film 2 is formed on a silicon substrate 1, and a photolithography step and an ion

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implantation step are successively performed to form an N type well region 3 and a P type well region 4 in the substrate 1. For instance, phosphorous is ion-implanted at approximately  $1 \times 10^{13}$  atmos/cm<sup>2</sup> to form the N type well region 3, and boron is ion-implanted  
5 at approximately  $3.4 \times 10^{13}$  atmos/cm<sup>2</sup> to form the P type well region 4.

Next, after a heat treatment called as drive-in is performed at 1170°C, as shown in FIG. 1B, a nitride film (Si<sub>3</sub>N<sub>4</sub>) 5 is deposited on the silicon substrate 1 by a low pressure CVD method. After  
10 that, the nitride film 5 is patterned. After a resist is disposed and patterned by a photolithography step, boron is ion-implanted, for instance, at  $7 \times 10^{13}$  atmos/cm<sup>2</sup> into a region where a channel stopper 6 is to be formed. Then, annealing is performed in N<sub>2</sub> atmosphere to form the channel stopper 6.

15 As shown in FIG. 1C, a LOCOS oxide film 7 is formed by thermal oxidation for element isolation at a boundary portion between the N type well region 3 and the P type well region 4. The nitride film 5 and the oxide film region other than the LOCOS oxide film 7 are removed. As shown in FIG. 2A, a gate oxide film 8 is further  
20 formed by thermal oxidation. The method for measuring the thickness of the oxide film according to the present invention is applied to this gate oxide film 8.

Specifically, the thickness of the gate oxide film 8 is measured by an ellipsometer utilizing a polarization analysis.  
25 That is, light is irradiated on the gate oxide film 8 and a refractive index and an absorption coefficient of the gate oxide film 8 are detected to determine the thickness of the gate oxide film 8.

This measurement of the thickness is performed when a specific period of time is elapsed from the time when the gate oxide film 8 is formed.

10 This is because it is found that an apparent thickness of the oxide film measured by an optical instrument increases gradually after the oxide film is formed on the substrate. FIG. 3 shows a relation between a change in apparent thickness of the oxide film and a left period of time from the time immediately after the oxide film is formed to the time for measuring the thickness. As shown in the figure, the apparent thickness of the oxide film changes in accordance with the left period of time after the oxide film is formed. The longer the left period of time becomes, the larger the thickness of the oxide film becomes apparently. This phenomenon is considered as follows.

15 As described above, the thickness of the oxide film is determined based on the refractive index and the absorption coefficient detected by light irradiated on the oxide film. That is, the thickness of the oxide film is measured based on the change in light incident on the oxide film. Therefore, if deposits exist  
20 on the surface of the oxide film to influence the refractive index and the like, the thickness of the oxide film can be measured as if it is increased.

To confirm this point, the surface of the oxide film, a thickness of which was increased apparently, was washed, and then  
25 the thickness of the oxide film was measured again. As a result, the thickness of the oxide film was returned to that measured immediately after the oxide film was formed. This reveals that

deposits (for instance, water and carbon in the air) attached to the surface of the oxide film can apparently increase the thickness of the oxide film.

Incidentally, after the surface of the oxide film was washed, the oxide film was left for a specific period of time again, and the change in thickness of the oxide film was measured with respect to the left period of time. Consequently, substantially the same experimental result as that shown in FIG. 3 was obtained. This result supports that water, carbon, and the like in the air are attached to the surface of the oxide film to apparently increase the thickness of the oxide film when the oxide film is left.

In view of the points described above, in the present embodiment, the time for measuring the thickness of the gate oxide film 8 is controlled, and the thickness of the gate oxide film 8 is measured within a specific period of time elapsed after the gate oxide film 8 is formed. Accordingly, the thickness of the gate oxide film 8 can be measured accurately before it is increased apparently.

The shorter the period of time for measuring the thickness is, the more the thickness of the gate oxide film is measured accurately. The period of time for measurement may be determined as follows.

For instance, an allowable thickness variation with respect to latitude (specification) for process control can be calculated to determine the period of time for measurement. The thickness variation in the process is calculated by a formula of:

$$\sqrt{S^2 + T^2} \leq U' \quad \dots\dots(1)$$

where S is a variation in thickness of the gate oxide film, T is a change-variation in thickness of the gate oxide film according to the left period of time, and U is a specification latitude for the process control. The variation is calculated at  $3\sigma$ . The variation S is produced when the gate oxide film is formed.

The width of the variation T that fulfills the formula (1) can determine the specific period of time for measuring the thickness based on the experimental result. The width of variation may be determined using an approximate formula that is explained in a second embodiment below.

Accordingly, after the thickness of the gate oxide film is measured, the next step is carried out when the thickness falls in a desirable range. If the thickness is out of the range, the product is removed from the manufacture line. Thus, the thickness of the gate oxide film 8 can be measured accurately by controlling the period of time for the measurement such that the measurement is performed in a short time from the formation of the gate oxide film 8. By performing the measurement of the thickness in the present embodiment, defectives can be found out on the way of manufacture with high accuracy, resulting in quick feedback for process improvement and stable yield.

As to the product fit in the thickness, as shown in FIG. 2A, a gate electrode 9 is formed and patterned on the gate oxide film 8. Successively, as shown in FIG. 2B, after a source 10 and a drain 11 are formed at both sides of the gate electrode 9, a CVD oxide film 12 is formed on the surface of the silicon substrate 1 to cover the gate electrode 9. After a reflow treatment is



performed, contact holes 12a are formed in the CVD oxide film 12. An electrical wiring pattern 13 is then disposed not only on the CVD oxide film 12 but in the contact holes 12a, and is covered by a protective film not shown. As a result, the MOS transistor is completed.

(Second Embodiment)

In a second preferred embodiment, a thickness of an oxide film, which has been measured apparently, is corrected so that an accurate thickness of the oxide film is obtained. An object to which the method for measuring the thickness of the oxide film is applied in the second embodiment is substantially the same as the MOS transistor in the first embodiment. The process for checking product defectives based on the measured thickness of the oxide film is also substantially the same as that in the first embodiment. Mainly, the correction of the thickness is explained below.

As described above, when the gate oxide film 8 is left after its formation, the relation between the apparent thickness of the gate oxide film and the left period of time is as shown in FIG. 3. An increase in the apparent thickness of the gate oxide film is represented by an approximate formula of:

*and a*

$$y = a \cdot \ln(t) + b \quad \dots\dots(2)$$

where  $t \geq 1$ , and an unit of  $y$  is Å.

*and ag*

In the formula (2), "a" and "b" are constants, and "t" is a left period of time elapsed from the formation of the gate oxide film 8 to the measurement of the thickness. The constant a is determined by atmosphere (temperature, moisture) around a wafer

disposed within a clean room, or the like, and was in a range of approximately 0.5 to 1.5 when it was measured in practice. The constant  $b$  is a thickness of the oxide film measured immediately after the gate oxide film 8 is formed (when  $t = 1$  min).

5           Incidentally, if the left period of time  $t$  was set to be zero in the formula (2), the thickness of the gate oxide film calculated by the formula (2) is  $0\text{\AA}$ . This means that the gate oxide film 8 does not exist. Therefore, the left period of time  $t$  cannot be set to be less than 1 min when the thickness is measured immediately after the gate oxide film is formed. In practice, the initial thickness of the gate oxide film 8 is measured after the wafer is taken out of an apparatus for forming the oxide film 8. Because of this, approximately 1 min or more is required to measure the initial thickness of the gate oxide film 8 from the formation of the gate oxide film 8. Therefore, the approximate formula (2) meets the practical use.

Accordingly, the apparent increase in thickness of the gate oxide film 8 is approximated by the formula (2), and calculated in accordance with the left period of time after the formation of the gate oxide film 8. The thickness of the gate oxide film can be corrected by subtracting the apparent increase in thickness from the measured apparent thickness of the gate oxide film. Thus, the left period of time is controlled after the gate oxide film 8 is formed, and the apparent thickness of the gate oxide film is corrected by the approximate formula (2). Consequently, the accurate thickness of the gate oxide can be detected.

FIG. 4 shows variations in thickness of the gate oxide film,

quantified by the approximate formula (2) for reference. The result shown in FIG. 4 was obtained by leaving plural samples (samples A-J) for various periods of time, measuring the thickness of the gate oxide film in each sample by an ellipsometer, and correcting the measured result by the formula (2). In the figure, a broken line indicates the measured apparent thicknesses, and a solid line indicates the thicknesses of the gate oxide film after correction. Each left period of time for each sample is shown above each alphabetical reference.

10 As shown in the figure, the measured thickness has large variations. As opposed to this, the thickness after correction has significantly decreased variations. This implies that, when the correction is not performed by the approximate formula, the measured thickness is accompanied by large variations regardless  
15 of its actual thickness falling in the desirable range. In such a case, the thickness of the gate oxide film might be determined to be out of the range erroneously. The correction of the gate oxide film thickness using the formula (2) can prevent such erroneous determination.

20 Further, reliability of the gate oxide film thickness corrected by the approximate formula was evaluated while being compared with the gate oxide film thickness that was estimated by a capacitance (capacitance produced between the gate electrode and the silicon substrate) after the product was manufactured.  
25 The comparing result is shown in FIG. 5. The thicknesses measured by the ellipsometer and not corrected, i.e., the thicknesses before correction, are also plotted in the figure for reference.

As shown in the figure, the thickness of the gate oxide film corrected by the approximate formula approximately corresponds to that obtained by the capacitance, and has a significant correlation therewith. On the other hand, the thickness of the gate oxide film before correction has no relation with that obtained by the capacitance. Thus, it is confirmed that the correction using the approximate formula can determine the thickness of the gate oxide film with high reliability and high accuracy.

(Third Embodiment)

As described above, deposits on the surface of the gate oxide film 8 can cause variations in apparent thickness of the film 8. Therefore, in a third preferred embodiment, deposits are removed from the surface of the gate oxide film 8 so that the thickness of the film 8 can be measured accurately. An object to which the present embodiment is applied is substantially the same as the MOS transistor as in the first embodiment, and the method for checking product defectives based on the measured thickness of the gate oxide film is also substantially the same as that in the first embodiment. Mainly explained below is a method for removing deposits from the surface of the gate oxide film 8.

First, the gate oxide film 8 is formed on the silicon substrate 1 by performing the steps substantially the same as those in the first embodiment. Then, immediately before the thickness of the gate oxide film is measured, the surface of the gate oxide film 8 is washed by a washing solution so that deposits are removed

from the surface. Specifically, the wafer is immersed into a washing solution (mixed solution) of sulfuric acid ( $H_2SO_4$ ) and hydrogen peroxide ( $H_2O_2$ ), so that deposits are removed from the wafer. After that, the thickness of the gate oxide film is measured.

5 The thickness of the gate oxide film can be measured without being affected by the deposits, resulting in accurate measurement of the thickness.

FIG. 6A shows thicknesses of the gate oxide film measured before and after the removal of deposits. Specifically, the  
10 thickness of the gate oxide film was measured after 49 min and 16067 min were respectively elapsed from the formation of the gate oxide film 8, and after 50 min was elapsed from the washing using the mixed solution of  $H_2SO_4$  and  $H_2O_2$ . The results are shown in FIG. 6A.

15 As shown in the figure, the gate oxide film, which is left for a long period of time after its formation, has an apparently increased thickness, as compared to that immediately after the gate oxide film is formed (when left period of time is 49 min). As opposed to this, the washing using the mixed solution of  $H_2SO_4$   
20 and  $H_2O_2$  can return the measured thickness of the gate oxide film 8 to approximately its initial value where the oxide film 8 is not left for a long period of time. The experimental results also reveal that the thickness of the gate oxide film 8 can be measured accurately by removing deposits from the surface of the gate oxide  
25 film 8 immediately before the thickness is measured.

Incidentally, after the wafer was left for a specific period of time after the washing step was performed, the thickness of

the gate oxide film was measured again. The thickness of the gate oxide film was increased in a similar relation to that increased by being left before the washing step was performed. This result supports that the increase in the apparent thickness of the gate oxide film is caused by deposits of matters, which are contained in the air, on the surface of the gate oxide film. The deposits can change slightly a refractive index, and the like.

Thus, according to the present embodiment, the thickness of the gate oxide film can be measured accurately without being affected by deposits, by removing the deposits from the surface of the gate oxide film. In addition, in the present embodiment, even when the left period of time of the wafer before washing is not known, the thickness of the gate oxide film can be measured accurately by controlling the left period of time after washing.

Incidentally, as described above, since the apparent thickness of the gate oxide film is increased after washing, the thickness should be measured in a specific period of time after washing, as in the first embodiment. In the present embodiment, although deposits are removed by the washing using the mixed solution of  $H_2SO_4$  and  $H_2O_2$ , other washing solutions such as a mixed solution of hydrochloric acid (HCl) and  $H_2O_2$  (HPM solution) may be used in place of the mixed solution of  $H_2SO_4$  and  $H_2O_2$ .

FIG. 6B shows measurement results of gate oxide film thicknesses before and after removing deposits by the mixed solution of HCl and  $H_2O_2$ , similarly to those in FIG. 6A. As shown in the figure, when the mixed solution of HCl and  $H_2O_2$  is used as a washing solution, the same effects as those of the mixed

solution of  $H_2SO_4$  and  $H_2O_2$  are provided.

According to these results obtained by the washing using the mixed solution of  $H_2SO_4$  and  $H_2O_2$  and the washing using the mixed solution of  $HCl$  and  $H_2O_2$ , it is considered that water and carbon, which are contained in the air and are liable to be dissolved in or react with sulfuric acid ( $H_2SO_4$ ) or hydrochloric acid ( $HCl$ ), are attached to the surface of the gate oxide film to increase the apparent thickness of the gate oxide film. Therefore, any washing solution can be used provided that it can remove water and carbon from the surface of the oxide film.

In the embodiments described above, the gate oxide film is formed through wet oxidation by a thermal CVD method. However, it is confirmed that the same effects as those in the embodiments described above were provided even when the gate oxide film was formed by other methods such as dry oxidation and plasma CVD method. The present invention can be applied to gate oxide films formed by various methods. In the second embodiment, although the apparent thickness of the gate oxide film is approximated by the formula (2), it can be approximated by other formulas (for instance, approximate formula using logarithm).

In the embodiments described above, the thickness of the gate oxide film is in a range of approximately  $90\text{\AA}$  to  $110\text{\AA}$ . However, the present invention is especially effective when the thickness of the gate oxide film is less than approximately  $100\text{\AA}$ . The thinner the oxide film is, the more the rate of change-variations in the thickness is prominent. Therefore, in such a case, the thickness control according to the present

invention is very effective to measure the real thickness precisely.

It is apparent that the present invention can be applied to the gate oxide film more than 100 Å in thickness as well.

While the present invention has been shown and described  
5 with reference to the foregoing preferred embodiments, it will  
be apparent to those skilled in the art that changes in form and  
detail may be made therein without departing from the scope of  
the invention as defined in the appended claims.